Mixed-metal Cluster Compounds containing Copper and/or Silver Atoms Ligated by Mono- or Bi-dentate Phosphines: A Versatile High Yield Synthetic Route

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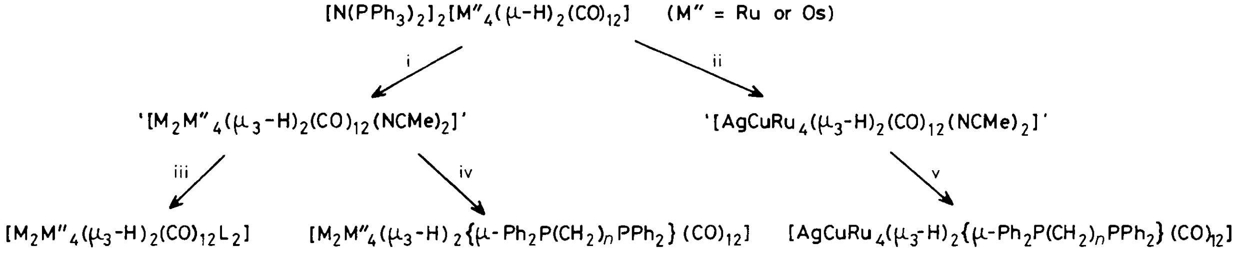
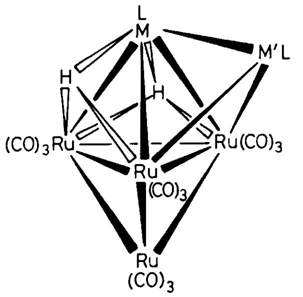
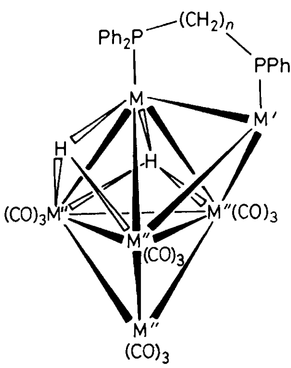
A wide variety of mixed-metal cluster compounds containing one or two copper and/or silver atoms ligated by a large selection of mono- or bi-dentate phosphines can be synthesized in very good yield (*ca.* 70—80%) by first treating an appropriate preformed cluster mono- or di-anion with one or two equivalents, respectively, of the complex $[M(NCMe)_4]PF_6$ (M = Cu or Ag) to incorporate the coinage metal(s) into the cluster in the form of M(NCMe) moieties and then attaching the desired phosphine *in situ,* by a ligand exchange reaction with the labile MeCN group(s) on the generally unstable intermediate species.

The considerable recent interest shown in mixed-metal cluster compounds containing one or more gold atoms, especially species in which $Au(PR_3)$ (R = aryl or alkyl) fragments are incorporated into structures containing a number of ruthenium or osmium atoms ligated by carbonyl groups, has led to the discovery of novel chemistry.[1] However, reports of analogous species containing copper or silver are still relatively rare[2—5] and examples of heteronuclear clusters containing two different coinage metals are even more scarce,[2] despite the fact that the results published so far suggest that the chemistry of these species will be as varied and interesting as that of their gold analogues.[2—5] Almost all known copper or



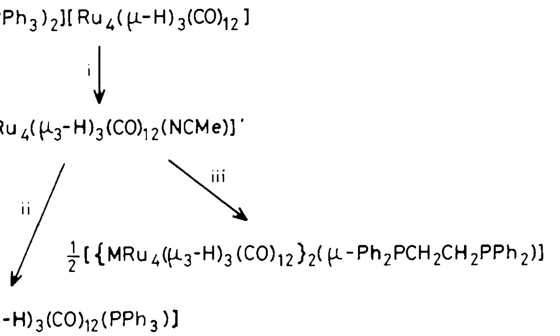
Scheme 1. *Reagents:* (CH_2Cl_2 solutions at −30 °C) i, $[M(NCMe)_4]PF_6$ (M = Cu or Ag) (2 equiv.); ii, $[Cu(NCMe)_4]PF_6$ (1 equiv.) and $[Ag(NCMe)_4]PF_6$ (1 equiv.); iii, L (M = Cu, L = PPh_3, PMe_2Ph or PEt_3; M = Ag, L = PPh_3 or $PMePh_2$) (2 equiv.); iv, $Ph_2P(CH_2)_nPPh_2$ (n = 1—6) (1 equiv.); v, $pH_2P(CH_2)nPPh_2$ (n = 1 or 2) (1 equiv.).



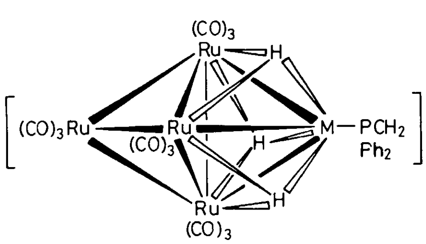


(**1**) M = M' = Cu, L = PPh_3
(**2**) M = M' = Ag, L = PPh_3
(**5**) M = M' = Cu, L = PMe_2Ph
(**6**) M = M' = Cu, L = PEt_3
(**7**) M = M' = Ag, L = $PMePh_2$

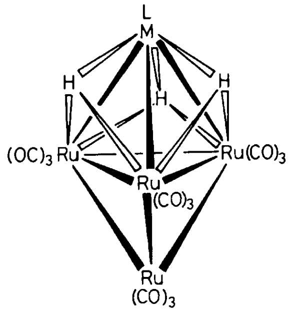
M = M' = Cu, M" = Ru:
(**3**) *n* = 1
(**4**) *n* = 2
(**8**) *n* = 3
(**9**) *n* = 4
(**10**) *n* = 5
(**11**) *n* = 6
M = M' = Ag, M" = Ru:
(**12**) *n* = 1
(**13**) *n* = 2
(**14**) *n* = 3
(**15**) *n* = 4
(**16**) *n* = 5
(**17**) *n* = 6
(**18**) M = M' = Cu, M" = Os, *n* = 2
(**19**) M = M' = Ag, M" = Os, *n* = 2
M = Cu, M' = Ag, M" = Ru:
(**20**) *n* = 1
(**21**) *n* = 2.



Scheme 2. *Reagents:* (CH_2Cl_2 solutions at −30 °C) i, $[M(NCMe)_4]PF_6$ (M = Cu or Ag) (1 equiv.); ii, PPh_3 (1 equiv.); iii, $Ph_2PCH_2CH_2PPh_2$ (0.5 equiv.).



(**22**) M = Cu.
(**23**) M = Ag.



(**24**) M = Cu, L = PPh_3.
(**25**) M = Ag, L = PPh_3

silver heteronuclear clusters containing phosphine ligands have been prepared by treating a polynuclear metal-carbonyl anion with an appropriate amount of the complex $[MX(PR_3)]$ (M = Cu or Ag; X = Cl or I; R = aryl or alkyl), sometimes in the presence of $TlPF_6$.[2—4] However, two problems are encountered with this synthetic approach. Firstly, although the reported yields lie in the range *ca.* 30—70%, typical results are nearer to the lower figure.[2—4] Secondly, we have found that this route is rather inflexible, because of the severe problems which arise when the group 1B metal halide complex of a desired ligand is not available, unstable, or has very poor solubility in common organic solvents. Herein we describe the details of a very versatile preparative procedure which allows a wide variety of mixed-metal clusters containing one or more copper and/or silver atoms ligated by a large selection of mono- or bi-dentate phosphines to be synthesized for study in *ca.* 70—80% yield. The new route is superior, because it not only offers yields which are frequently substantially better than those obtained using the original approach, but it also avoids the difficulties described above, since the coinage metal(s) are first introduced into the cluster in the form of M(NCMe) (M = Cu or Ag) units by treating a preformed cluster anion with the appropriate amount of the complex $[M(NCMe)_4]PF_6$ and then the desired phosphine is attached *in situ* by a ligand exchange reaction with the labile MeCN group(s) on the generally unstable intermediate species.

The preparations shown in Scheme 1 provide a good example to demonstrate the flexibility and other advantages of the new synthetic procedure. One of us has previously reported[2] the synthesis of the bimetallic hexanuclear clusters $[M_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ [(**1**), M = Cu; (**2**), M = Ag] in *ca.* 50% yield, by treating the salt $[N(PPh_3)_2]_2[Ru_4(\mu\text{-}H)_2(CO)_{12}]$ with $[MX(PPh_3)]$ (M = Cu, X = Cl; M = Ag, X = I), in the presence of $TlPF_6$. However, our attempts to prepare the closely related species $[Cu_2Ru_4(\mu_3\text{-}H)_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}(CO)_{12}]$ [(**3**), *n* = 1; (**4**), *n* = 2] in a similar manner, using the complexes $[Cu_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}Cl_2]$ in place of $[CuCl(PPh_3)]$, resulted in yields of 25 and 12% for (**3**) and (**4**), respectively. It seems that these low yields are due to the very poor solubility of the phosphine copper halide species in all suitable organic solvents. However, these solubility problems are completely avoided by the new two step route (Scheme 1). Initially, treatment of a CH_2Cl_2 solution of the salt $[N(PPh_3)_2]_2[M''_4(\mu\text{-}H)_2(CO)_{12}]$ (M" = Ru[6] or Os[7]) at −30 °C with two equivalents of the complex $[M(NCMe)_4]PF_6$ (M = Cu or Ag) incorporates two M(NCMe) units into the cluster anion. This type of synthetic approach has been previously reported[8] as a route to a small number of heteronuclear clusters containing one or two Cu(NCMe) moieties, but, in this case, the intermediate clusters are too unstable to isolate. However, the lability of the MeCN groups on these intermediate species can be readily utilized to attach the desired mono- or bi-dentate phosphine ligand to the coinage metals and the relatively stable phosphine-containing clusters (**1**)—(**19**) can then be easily purified by column chromatography at −20 °C on alumina or Florisil. Interestingly, the same synthetic approach can be extended to prepare the unusual trimetallic clusters $[AgCuRu_4(\mu_3\text{-}H)_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}(CO)_{12}]$ [(**20**), $n = 1$; (**21**), $n = 2$] by using a CH_2Cl_2 solution containing a mixture of one equivalent of $[Cu(NCMe)_4]PF_6$ and one equivalent of $[Ag(NCMe)_4]PF_6$ in the first step (Scheme 1). Furthermore, the general preparative procedure can equally well be used to synthesize heteronuclear clusters containing a single copper or silver atom and even to link two such units together with a bidentate phosphine ligand, as illustrated in Scheme 2 for the new compounds (**22**) and (**23**) and the previously reported[3] species (**24**) and (**25**).†

Although all of the example clusters described herein have phosphine ligands attached to the coinage metal(s), it seems likely that the new synthetic route will eventually prove to be even more versatile. In principle, there is no reason why any mono- or bi-dentate ligand should not be attached to group 1B metal heteronuclear clusters in the same way, given that the final product is sufficiently stable to isolate, allowing a wide variety of novel species to be prepared for study. In addition, the preparative technique may well also prove to be a very convenient general method for bonding copper and silver heteronuclear clusters to phosphine-functionalized solid supports, such as alumina or silica.

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† Satisfactory spectroscopic and analytical data were obtained for all of the new mixed-metal cluster compounds.